PATENT SPECIFICATION

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565,991

PROVISIONAL SPECIFICATION

Removal of Oxygen from Olefines

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention (which has been communicated to us by E. I. Du Pont de Nemours and Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America,) to be as follows:—

This invention relates to a method for removing oxygen from gaseous olefines, especially ethylene, containing small proportions of oxygen generally less than 1% by volume.

In various chemical processes involving the use of gaseous olefines it has been found necessary to remove partially or completely the oxygen content of the gas. For instance, in the polymerisation of olefines such as ethylene even less than 0.1% of oxygen has a marked effect upon the polymerisation reaction. The object of this invention is to provide a new and improved method for the partial or complete removal of oxygen from olefines containing it, especially from ethylene.

It is known that mixtures containing substantial proportions of ethylene and oxygen can be reacted at temperatures of 150°—400° C. and pressures of 1—50 atmospheres, and that this reaction can be carried out in the presence of catalysis. Such work does not show whether oxygen can be removed from ethylene containing only small proportions of it. It is also known that oxygen can be removed from hydrogen at atmospheric or slightly elevated pressure by vapour phase reaction over many types of catalyst; this reaction involves in some way the production of water vapour. When one tries to remove oxygen from olefines in the same manner the catalyst becomes oxidised and thereafter the reaction slows down or stops altogether, and the catalyst requires periodic reduction by hydrogen. This can be avoided to some extent by the presence of considerable quantities of hydrogen in the olefine gas, but such quantities of hydrogen are not always desirable. We have now found that periodic reduction of the catalyst by hydrogen is no longer necessary if the removal of oxygen from the olefine gas is carried out at a high pressure.

According to the present invention, we provide a process for the partial or complete removal of oxygen from oxygen-containing gaseous olefines particularly ethylene, which comprises passing the said gas at an elevated pressure through one or more vessels containing catalysts of the type which are suitable for the catalytic removal of oxygen from hydrogen. We prefer to employ two or more catalyst vessels with one or more intervening traps which may contain a chemical or physical absorbent.

When two or more catalyst vessels are used with traps between, the traps remove one or more products of the reaction which has occurred in the preceding catalyst vessel. Such products if not removed apparently have a deleterious effect on the reaction in the succeeding catalyst vessel. If desired, the traps may contain various chemical or physical absorbents such as caustic soda or caustic potash, alumina gel, silica gel, active charcoal and the like, preferably alumina gel.

The efficiency of oxygen removal depends *inter alia* on the pressure employed and on the catalyst selected. Amongst catalysts which are suitable for the catalytic removal of oxygen from hydrogen we prefer to employ in the present process metals, metal oxides, reduced metal oxides or mixtures thereof which are known to be operative for the catalytic removal of oxygen from hydrogen at temperatures of 50°—300° C. In particular we prefer to use the metals and oxides of copper, nickel, silver, gold, platinum and palladium. The pressure required is determined largely by the catalyst, the temperature, and the composition of the olefine gas; copper and nickel catalysts require higher pressures generally than platinum and palladium. We prefer to employ pressures of 100—2000 atmospheres, and temperatures of 30°—150° C., but higher or lower pressures and temperatures may be used. At

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a pressure of about 100 atmospheres a temperature of 150° C. is necessary for satisfactory rates of reaction, and at a pressure of 1000 atmospheres temperatures below 100° C. should generally be used because higher temperatures cause undesirable reactions and polymerisations which interfere with the process. By carrying out the process at a high pressure such as 1000 atmospheres and a moderate temperature such as 50°—100° C., the rate of reaction is high and the activity of the catalyst is maintained for long periods.

The invention is illustrated but not restricted by the following examples, in which the parts per million are measured by volume. By the term space velocity is meant the volume of gas measured at 20° C. and 1 atmosphere pressure per hour per volume of converter (or catalyst tube) space.

EXAMPLE 1.

A steam-jacketed pressure-resistant copper-lined catalyst tube of 100 cc. capacity and fitted with a thermo-couple and high pressure connections, was filled with granular reduced copper oxide. The catalyst was maintained at 90° C., and ethylene containing 180 parts per million of oxygen was passed in at a pressure of 1000 atmospheres and a space velocity of 1200. The issuing ethylene contained 52 parts per million of oxygen and the catalyst did not require periodic reactivation by reduction with hydrogen.

EXAMPLE 2.

Ethylene containing 1000 parts per million of oxygen was passed at a pressure of 1000 atmospheres and a temperature of 30° C. over catalytically active Raney nickel. The issuing gas contained only 400 parts per million of oxygen, and the catalyst did not require periodic reactivation by reduction with hydrogen.

Dated the 2nd day of April, 1943.

E. A. BINGEN,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Removal of Oxygen from Olefines

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention (which has been communicated to us by E. I. Du Pont de Nemours and Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method for removing oxygen from gaseous olefines, especially ethylene, containing small proportions of oxygen generally less than 1% by volume.

In various chemical processes involving the use of gaseous olefines it has been found necessary to remove partially or completely the oxygen content of the gas. For instance, in the polymerisation of olefines such as ethylene even 0.005—0.1% of oxygen has a marked effect upon the polymerisation reaction. The object of this invention is to provide a new and improved method for the partial or complete removal of oxygen from gaseous olefines containing it, especially from ethylene.

It is known that mixtures containing at least several percent. of each of ethylene and oxygen can be reacted at temperatures of 150°—400° C. and pressures of 1—50 atmospheres, and that this reaction can be carried out in the presence of catalysts. Such work does not show whether oxygen can be removed from mixtures containing substantial proportions of ethylene and only small proportions of oxygen. It is also known that oxygen can be removed from hydrogen at atmospheric or slightly elevated pressure by vapour phase reaction over many types of catalyst; this reaction involves in some way the production of water vapour. When one tries to remove oxygen from olefines in the same manner the catalyst becomes oxidised and thereafter the reaction slows down or stops altogether, and the catalyst requires periodic reduction by hydrogen. This can be avoided to some extent by the presence of considerable quantities of hydrogen in the olefine gas, but such quantities of hydrogen are not always desirable. We have now found that periodic reduction of the catalyst by hydrogen is no longer necessary, or at least only necessary at less frequent intervals, if the removal of oxygen from the olefine gas is carried out at a high pressure.

According to the present invention, we provide a process for the partial or complete removal of oxygen from gaseous mixtures consisting substantially of

olefines particularly ethylene and a small proportion of oxygen, which comprises passing the said mixture at an elevated pressure not less than 20 atmospheres through one or more vessels containing as catalyst one or more of the following metals or oxides thereof: copper, nickel, silver, gold, platinum and palladium. We prefer to employ two or more catalyst vessels with one or more intervening traps which may contain a chemical or physical absorbent in accordance with the process claimed in British Specification No. 560,497.

The efficiency of oxygen removal depends *inter alia* on the pressure employed and on the catalyst selected. We prefer to use the reduced oxides of copper or nickel because of their relatively low cost. They are highly active when in the form of reduced granular fused oxide.

The pressure required is determined largely by the catalyst, the temperature, and the composition of the olefine gas; copper and nickel catalysts require higher pressures generally than platinum and palladium. Although these metals in the active state such as the reduced metal oxides are effective at quite low pressures such as 1—10 atmospheres in removing oxygen, they normally require periodic reactivation by reduction with hydrogen under such conditions. By raising the pressure this periodic reactivation becomes unnecessary or at least only necessary at less frequent intervals. We prefer to employ pressures of 50—2000 atmospheres, and temperature of 30°—150° C., but pressures as low as 20 atmospheres and temperatures as high as 200° C. may be used. At a pressure of 20—100 atmospheres a temperature of 100°—200° C. gives satisfactory reaction with copper and nickel catalysts, and at a pressure of 1000 atmospheres temperatures not exceeding 100° C. should generally be used because higher temperatures cause undesirable reactions and polymerisation of the olefines which interfere with the present process. A combination of high temperature such as 200° C. with high pressure such as 1000 atmospheres should generally be avoided because the catalyst may become fouled with a polymeric product during a few hours working. By carrying out the process at a high pressure such as 100—1000 atmospheres and a moderate temperature such as 30°—100° C., the rate of reaction is high and the activity of the catalyst is maintained for long periods. A suitable rate of reaction is a space velocity of 500—20,000 as this rate provides efficient operation and a high output.

When two or more catalyst vessels are used with traps between, the traps remove one or more materials, generally colourless liquids, which are products of a reaction which has occurred in the preceding catalyst vessel. Such products if not removed apparently have a deleterious effect on the reaction in the succeeding catalyst vessel. If desired, the traps may contain various chemical or physical absorbents such as caustic soda or caustic potash, alumina gel, silica gel, active charcoal and the like, preferably alumina gel. The traps are generally maintained at a lower temperature than the temperature of the catalysts, especially when the traps do not contain any chemical or physical absorbent.

We believe that the catalyst causes an incomplete equilibrium reaction to occur, and when we have two catalyst vessels separated by a trap further reaction occurs in the second catalyst chamber due to the removal in the trap of a product which is condensible at a temperature below that of the catalyst, or which is absorbed by an absorbent. This is borne out by the fact that varying amounts of moisture or other absorbed material or both have been distilled from the absorbent in the traps after extended use. The amount of oxygen removed in passage through each tube is generally about 65—75% of the total oxygen content entering that tube. The number of catalyst tubes, with alternate traps, in a given oxygen-removal operation depends, therefore, upon the amount of oxygen present in the gas to be purified, and on the amount which is permissible in the issuing gas.

The invention is applicable to gaseous mixtures containing high proportions of ethylene such as 80 to virtually 100%, and a small proportion of oxygen such as between 1% and a few parts per million. It may be used to prepare ethylene containing even as little as 1 part per million of oxygen.

The invention is illustrated but not restricted by the following examples, in which the parts per million are measured by volume. By the term space velocity is meant the volume of gas measured at 20° C. and 1 atmosphere pressure per hour per volume of converter (or catalyst tube) space.

EXAMPLE 1.

A steam-jacketed pressure-resistant copper-lined catalyst tube of 400 cc. capacity and fitted with a thermo-couple and high pressure connections, was filled with granular reduced copper oxide. The catalyst was maintained at 90° C., and ethylene containing 180 parts per million of oxygen was passed in at a pressure of

1000 atmospheres and a space velocity of 1200. The issuing ethylene contained 52 parts per million of oxygen and the catalyst did not require periodic reactivation by reduction with hydrogen.

EXAMPLE 2.

Ethylene containing 1000 parts per million of oxygen was passed at a pressure of 1000 atmospheres and a temperature of 30° C. over catalytically active Raney nickel. The issuing gas contained only 400 parts per million of oxygen, and the catalyst did not require periodic reactivation by reduction with hydrogen.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the removal of oxygen from gaseous mixtures consisting substantially of olefines especially ethylene and a small proportion of oxygen, which comprises passing the said mixture at an elevated pressure not less than 20 atmospheres through one or more vessels containing as catalyst one or more of the following metals or oxides thereof: copper, nickel, sliver, gold, platinum and palladium.

2. Process as claimed in claim 1 in which the pressure is between 50 and 2000 atmospheres.

3. Process as claimed in either of claims 1 and 2 in which the catalysts are maintained at a temperature of 30—150° C.

4. Process as claimed in any of the preceding claims in which copper or nickel catalyst is employed in the form of its reduced oxide.

5. Process for the removal of oxygen from gaseous mixtures consisting substantially of olefines and a small proportion of oxygen substantially as hereinbefore described with reference to each of the foregoing examples.

6. Ethylene whenever purified by the process of any of the preceding claims.

Dated the 13th day of March, 1944.

E. A. BINGEN,

Solicitor for the Applicants.

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